

ROTATIONAL EXCITATION OF HCN BY COLLISIONS

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ABSTRACT

Rate constants for rotational excitation of HCN by collisions with low-energy He atoms (kinetic temperatures below 100° K) have been computed from first principles. The accuracy of individual rates is conservatively estimated to be ± 50 percent above 30° K and within a factor of 2 below 20° K. These rates are also believed to be representative of excitation by collisions with H₂.

Subject headings: interstellar matter — molecules, interstellar — transition probabilities

With the recent discovery of interstellar molecules, it has become apparent that a significant fraction of galactic matter exists as interstellar molecular hydrogen which is invisible in all regions of the spectrum to ground-based observations and which has therefore been largely overlooked. On the other hand, a number of less abundant molecular species have been observed at radio wavelengths, particularly in the millimeter band. Since these species are believed to be associated with the H₂, such observations can be used to probe the physical conditions—e.g., the density and kinetic temperature—of the invisible H₂. Under conditions in a typical cloud, all molecules are in their lowest electronic and vibrational level and only a handful of rotational levels are significantly populated. Furthermore, since radiative transitions between rotational levels occur in these clouds about as frequently as collision-induced transitions, and since the radiative and collisional transitions obey different “selection rules,” the rotational levels are generally not in local thermodynamic equilibrium with either the radiation temperature or the ambient kinetic temperature. Thus, detailed knowledge of both radiative and collisional rates is necessary to understand the physics in these regions and to interpret the astronomical data. Whereas the radiative transitions are well understood, the relevant collision cross-sections can currently be measured only indirectly, if at all; and lack of accurately known values is a major obstacle to understanding interstellar clouds.

In principle, cross-sections for rotational excitation can be obtained directly from the equations of quantum theory. Although such calculations are generally quite difficult, some of the astrophysically important processes do seem amenable to current computational capability. The theoretical approach is conveniently divided into two independent parts: determination of the interaction potential, and calculation of the collision dynamics for this potential. The relevant computational techniques are discussed in detail in another paper where they are applied to

rotational excitation of CO by collisions with He and H₂ (Green and Thaddeus 1974). Because the calculations for HCN reported here use the same techniques found to be effective for CO, we will review only briefly the approximations used.

Calculations have been done only for HCN–He collisions. Since hydrogen molecules are presumably the main constituent of dense clouds, being 5 times more abundant than He atoms, the most important astrophysical process is HCN–H₂ collisions. However, HCN–He collisions are much simpler to treat theoretically. Also, at least for CO, it appears that excitation by collision with H₂ is quite similar to excitation by collision with He. While this may be less true for HCN, due to the long-range HCN–H₂ dipole-quadrupole interaction, the difference between He and H₂ projectiles is still expected to be no larger than the uncertainties introduced by other approximations. Furthermore, to a first approximation, HCN–H₂ cross-sections will be larger than those for HCN–He by a factor similar to that found for CO, an assumption whose validity should be reflected in the ratio of foreign-gas pressure broadening of HCN by H₂ and He.

For the scattering calculations HCN was assumed to be a linear rigid rotor with bond lengths set at the experimental values for the ground vibrational level,

TABLE 1
PARAMETERS USED TO COMPUTE THE LONG-RANGE HCN–He
INTERACTION POTENTIAL

Parameter	Units	HCN	He
Dipole moment.....	10^{-18} esu cm	3.0	...
Quadrupole moment....	10^{-26} esu cm ²	3.5	...
Ionization potential....	eV	14.8	24.5
Polarizability.....	Å ³	2.59	0.20
Polarizability, parallel to axis.....	Å ³	3.92	...
Polarizability, perpendicular to axis.....	Å ³	1.92	...

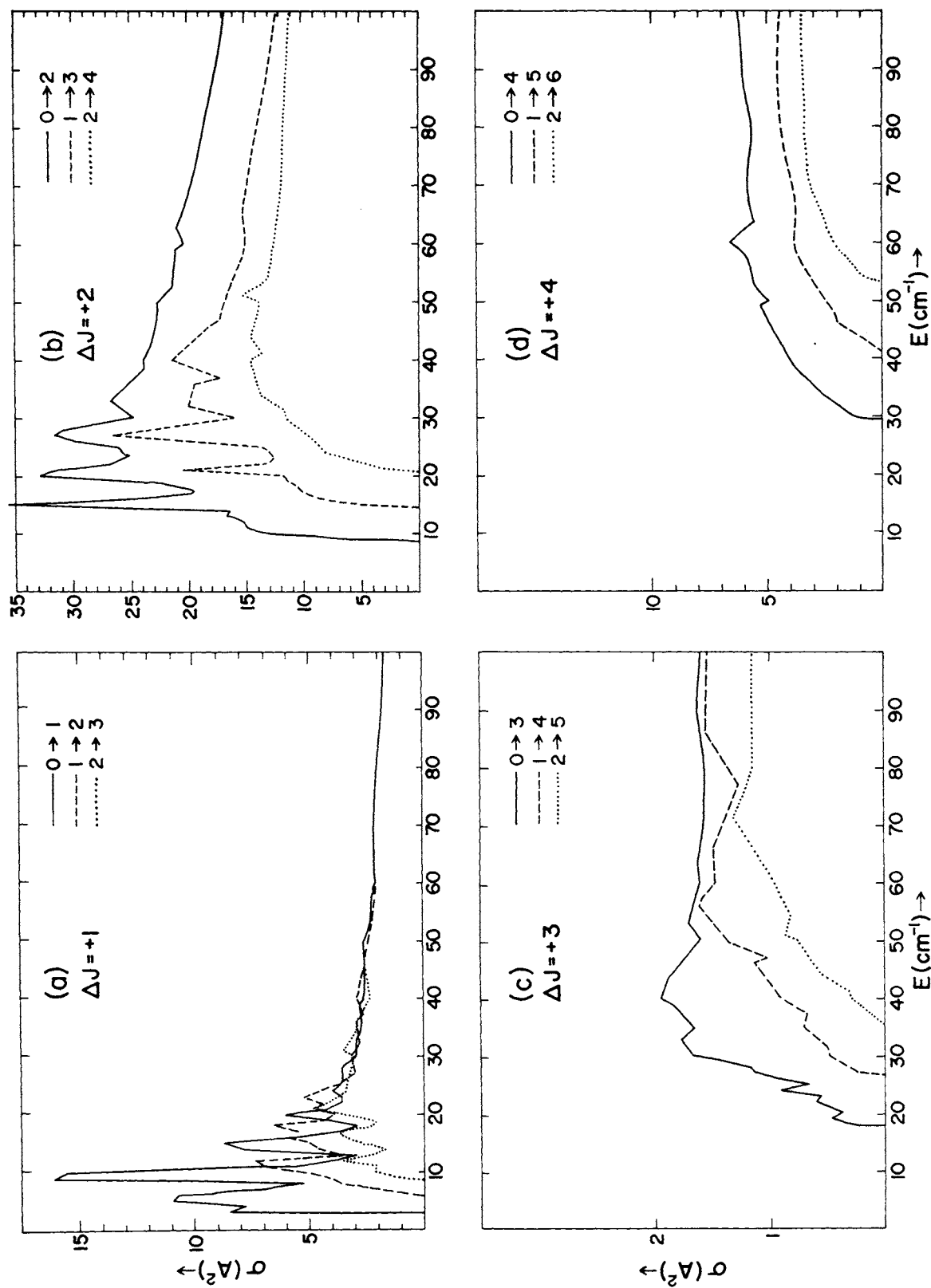


FIG. 1.—Computed cross-sections for rotational excitation of HCN by collision with He as a function of collision energy: (a) $\Delta J = +1$, (b) $\Delta J = +2$, (c) $\Delta J = +3$, and (d) $\Delta J = +4$.

TABLE 2
RATE COEFFICIENTS $R(j \rightarrow j')$ IN UNITS OF $10^{-10} \text{ cm}^3 \text{ s}^{-1}$

j	j'							
	0	1	2	3	4	5	6	7
$T = 5^\circ \text{ K:}$								
0.....	...	0.118	0.082	0.000	0.000	0.000	0.000	0.000
1.....	0.092	...	0.034	0.014	0.000	0.000	0.000	0.000
2.....	0.211	0.114	...	0.012	0.002	0.000	0.000	0.000
3.....	0.009	0.431	0.107	...	0.006	0.000	0.000	0.000
4.....	0.041	0.022	0.477	0.136	...	0.002	0.000	0.000
5.....	0.003	0.066	0.019	0.413	0.094	...	0.001	0.000
6.....	0.015	0.012	0.158	0.030	0.825	0.121	...	0.000
7.....	0.003	0.029	0.016	0.168	0.031	0.652	0.080	...
$T = 10^\circ \text{ K:}$								
0.....	...	0.157	0.336	0.006	0.006	0.000	0.000	0.000
1.....	0.080	...	0.085	0.130	0.002	0.001	0.000	0.000
2.....	0.241	0.120	...	0.044	0.048	0.000	0.000	0.000
3.....	0.012	0.467	0.113	...	0.028	0.019	0.000	0.000
4.....	0.045	0.025	0.521	0.121	...	0.018	0.010	0.000
5.....	0.005	0.090	0.029	0.553	0.124	...	0.012	0.004
6.....	0.015	0.012	0.152	0.038	0.776	0.130	...	0.007
7.....	0.003	0.034	0.019	0.192	0.047	0.769	0.122	...
$T = 20^\circ \text{ K:}$								
0.....	...	0.162	0.703	0.029	0.055	0.003	0.003	0.000
1.....	0.067	...	0.123	0.400	0.014	0.020	0.001	0.001
2.....	0.266	0.113	...	0.085	0.225	0.007	0.009	0.000
3.....	0.015	0.497	0.115	...	0.066	0.143	0.004	0.004
4.....	0.051	0.032	0.555	0.119	...	0.058	0.106	0.002
5.....	0.006	0.107	0.039	0.618	0.138	...	0.045	0.070
6.....	0.017	0.015	0.161	0.049	0.763	0.138	...	0.041
7.....	0.004	0.040	0.024	0.208	0.065	0.820	0.151	...
$T = 30^\circ \text{ K:}$								
0.....	...	0.158	0.903	0.049	0.121	0.010	0.013	0.001
1.....	0.061	...	0.134	0.580	0.030	0.059	0.005	0.005
2.....	0.276	0.107	...	0.105	0.379	0.018	0.034	0.003
3.....	0.016	0.505	0.115	...	0.088	0.278	0.012	0.020
4.....	0.055	0.036	0.569	0.121	...	0.084	0.230	0.011
5.....	0.008	0.116	0.045	0.635	0.140	...	0.071	0.176
6.....	0.020	0.018	0.169	0.056	0.758	0.141	...	0.074
7.....	0.004	0.045	0.029	0.214	0.077	0.816	0.163	...
$T = 40^\circ \text{ K:}$								
0.....	...	0.156	1.027	0.065	0.184	0.019	0.030	0.004
1.....	0.058	...	0.140	0.699	0.045	0.103	0.011	0.014
2.....	0.283	0.104	...	0.118	0.494	0.030	0.068	0.008
3.....	0.018	0.510	0.116	...	0.103	0.389	0.024	0.046
4.....	0.059	0.039	0.578	0.123	...	0.101	0.339	0.025
5.....	0.009	0.124	0.049	0.645	0.141	...	0.092	0.278
6.....	0.022	0.021	0.177	0.063	0.755	0.147	...	0.103
7.....	0.006	0.050	0.036	0.221	0.091	0.811	0.177	...
$T = 60^\circ \text{ K:}$								
0.....	...	0.153	1.175	0.088	0.293	0.039	0.075	0.018
1.....	0.055	...	0.148	0.847	0.069	0.188	0.029	0.045
2.....	0.291	0.102	...	0.133	0.654	0.052	0.138	0.027
3.....	0.019	0.518	0.118	...	0.122	0.550	0.050	0.106
4.....	0.066	0.044	0.598	0.126	...	0.124	0.502	0.060
5.....	0.010	0.138	0.056	0.663	0.145	...	0.128	0.439
6.....	0.026	0.027	0.191	0.078	0.758	0.166	...	0.154
7.....	0.009	0.060	0.052	0.236	0.120	0.809	0.208	...
$T = 100^\circ \text{ K:}$								
0.....	...	0.152	1.304	0.118	0.455	0.068	0.163	0.066
1.....	0.053	...	0.158	0.989	0.097	0.330	0.070	0.117
2.....	0.296	0.103	...	0.151	0.838	0.082	0.256	0.086
3.....	0.022	0.524	0.122	...	0.139	0.741	0.101	0.214
4.....	0.077	0.048	0.627	0.128	...	0.154	0.691	0.136
5.....	0.012	0.163	0.063	0.692	0.156	...	0.190	0.629
6.....	0.031	0.038	0.212	0.103	0.763	0.207	...	0.231
7.....	0.015	0.074	0.082	0.255	0.168	0.801	0.261	...

TABLE 3
 HCN-He INTERACTION POTENTIAL*

R	$v_0(R)$	$v_1(R)$	$v_2(R)$	$v_3(R)$	$v_4(R)$	$v_5(R)$	$v_6(R)$	$v_7(R)$	$v_8(R)$	$v_9(R)$
3.25.....	20,674.7	-10,646.9	40,907.9	-20,223.9	27,838.5	-18,067.6	15,668.9	-10,383.8	5947.2	-3782.8
3.50.....	14,239.6	-10,017.6	31,039.6	-18,162.6	23,393.4	-16,616.6	14,615.3	-10,174.6	5905.2	-3665.4
3.75.....	9378.6	-7780.4	21,675.3	-13,621.9	16,850.1	-12,257.9	10,667.4	-7539.7	4434.3	-2894.7
4.00.....	5893.3	-5231.6	14,103.0	-8997.0	10,941.7	-7799.4	6488.4	-4426.2	2447.8	-1499.0
4.25.....	3560.8	-3366.8	8756.8	-5591.2	6611.0	-4602.6	3697.3	-2358.8	1248.1	-628.6
4.50.....	2094.6	-2092.7	5347.9	-3352.1	3925.7	-2651.4	2072.2	-1324.6	669.7	-375.6
4.75.....	1189.9	-1267.0	3195.9	-1963.0	2288.2	-1472.6	1120.5	-699.0	339.6	-204.8
5.00.....	638.7	-760.9	1872.6	-1173.1	1342.0	-853.0	636.0	-364.2	172.3	-78.2
5.25.....	326.1	-469.2	1107.8	-724.4	828.3	-527.2	380.5	-209.0	90.5	-34.4
5.50.....	140.9	-268.2	613.7	-415.0	474.9	-302.4	217.3	-117.9	52.4	-17.6
5.75.....	41.1	-144.8	316.0	-228.1	268.7	-174.5	128.7	-82.1	59.1	-24.2
6.00.....	-9.5	-76.2	157.1	-123.5	143.8	-95.7	73.6	-43.6	28.3	-11.2
6.25.....	-30.0	-35.5	63.1	-63.7	77.4	-50.5	41.2	-31.4	23.2	-8.7
6.50.....	-34.7	-15.7	15.2	-27.4	35.6	-29.1	27.7	-18.1	12.4	-5.2
6.75.....	-33.9	-3.8	-5.1	-10.8	14.3	-16.0	13.6	-10.1	7.6	-1.6
7.00.....	-28.8	1.1	-9.9	0.3	4.5	-3.5	3.7	-7.2	1.8	-5.3
7.25.....	-24.6	1.7	-14.4	1.0	-0.2	-1.3	2.4	-2.3	0.0	0.0
7.50.....	-19.4	1.4	-12.3	0.7	-1.0	0.2	0.0	0.0	0.0	0.0
7.75.....	-15.4	3.1	-12.0	2.4	-2.7	0.7	0.0	0.0	0.0	0.0
8.00.....	-11.6	2.7	-9.7	2.2	-2.7	0.9	0.0	0.0	0.0	0.0
8.25.....	-9.8	2.1	-7.4	1.8	-2.3	0.8	0.0	0.0	0.0	0.0
8.50.....	-8.2	1.1	-5.6	1.5	-1.5	0.6	0.0	0.0	0.0	0.0
8.75.....	-6.9	0.9	-3.0	0.9	-1.3	0.6	0.0	0.0	0.0	0.0
9.00.....	-5.8	0.7	-2.1	0.5	-0.6	0.6	0.0	0.0	0.0	0.0
9.25.....	-4.9	0.6	-1.8	0.4	0.0	0.0	0.0	0.0	0.0	0.0

* $V(R, \theta) = \sum_{\lambda} v_{\lambda}(R) P_{\lambda}(\cos \theta)$, where $\theta = 0$ corresponds to the linear configuration HCN-He.

NOTE.—Distances are in atomic units and energies are in cm^{-1} .

$r_0(\text{HC}) = 1.064 \text{ \AA}$ and $r_0(\text{CN}) = 1.156 \text{ \AA}$ (Gordy and Cook 1970). Rotational energy levels were computed from $E_J = B_0 J(J+1)$ with $B_0 = 1.4783 \text{ cm}^{-1}$. The lowest vibrational frequency, that for the bending mode, is at 712 cm^{-1} (Townes and Schawlow 1955; the stretching modes are at 2041 and 3369 cm^{-1}). Thus excited vibrational states are not expected to be important for the low collision energies (less than about 300 cm^{-1}) considered here.

An ab initio potential energy surface was obtained using the uniform electron gas model of Gordon and Kim (1972). This method is relatively simple and economical, and appears to be reliable for closed-shell systems for separations around and inside the van der Waals potential minimum. However, its accuracy and range of validity, especially for molecule-atom interactions, are not yet completely established. Comparisons with experimental data have been favorable for $\text{N}_2\text{-Ar}$ (Kim 1973), HCl-Ar (Green 1974), and CO-He (Green and Thaddeus 1974). Studies are currently in progress to test this method against more accurate ab initio approximations. The angular dependence of the potential was analyzed into the usual Legendre series by a weighted least-squares procedure. For each interaction distance the potential was computed for as many as 19 angles, and up to 10 terms were retained in the Legendre expansion. The uniform electron gas approximation is known to fail at large separations because it includes neither induction nor dispersion forces. The ab initio potential was therefore joined smoothly to the asymptotic long-range perturbation theory potential between 4 and 5 \AA . The long-range terms were computed from equations given

by Green and Thaddeus (1974; cf. Buckingham 1967) and the molecular and atomic parameters given in table 1.

Collision dynamics were treated by the quantum close-coupling method (Arthurs and Dalgarno 1960). Extensive calculations were performed to check the dependence of computed cross-sections on the basis set size. (A basis set which includes HCN rotor levels $j = 0$ through $j = j_{\text{max}}$ is denoted by $B_{j_{\text{max}}}$.) Because of the highly anisotropic potential [terms through $P_6(\cos \theta)$ were larger than the spherical term] the convergence here was significantly worse than that found in previous calculations on other systems ($\text{H}_2\text{-Li}^+$, Lester and Schaefer 1973; CO-He , Green and Thaddeus 1974). For energies below 105 cm^{-1} the final calculations included at least two closed channels, a procedure which appears to give all cross-sections to within 10 percent of the infinite basis limit. Specifically, a B7 basis was used below 40 cm^{-1} , B8 was used between 40 and 80 cm^{-1} , and B9 was used between 80 and 130 cm^{-1} ; to estimate cross-sections at higher energies, a B7 basis was used. Selected cross-sections are shown in figure 1 as a function of collision energy. The cross-sections were averaged over Boltzmann energy distributions to obtain rate constants at temperatures between 5° and 100° K ; these are presented in table 2.

We believe that the greatest uncertainty in the computed HCN-He rate constants is due to inaccuracies in the interaction potential. (The potential used for these calculations is given in table 3.) For CO-He , experimental information was used both to correct for apparent inadequacies of the uniform

TABLE 4
PREDICTED PRESSURE-BROADENING CROSS-SECTIONS (\AA^2)

COLLISION ENERGY (cm^{-1})	TRANSITION		
	0-1	1-2	0-2
15.....	62.4	38.2	59.7
30.....	33.1	28.9	33.9
60.....	31.7	27.9	31.9
95.....	29.8	26.6	30.0
120.....	29.1	26.1	29.2
200.....	27.8	25.5	27.9
474.....	26.7	25.0	26.5
600.....	26.4	24.0	26.7
TEMPERATURE ($^{\circ}\text{K}$)			
77.....	35.7	31.0	35.8
100.....	34.4	30.3	34.5
200.....	28.9	26.1	29.0
300*.....	27.0	24.4	27.2

* Cohen and Wilson (1973) obtain $23 \pm 6 \text{\AA}^2$ from microwave measurements on vibrationally excited l -doublet transitions with $6 \leq j \leq 10$. A preliminary value (Nerf 1974) for the 0-1 transition is $29 \pm 6 \text{\AA}^2$.

electron gas model in the region of the potential well and also to place constraints on the computed inelastic cross-sections. Comparable data is not available for HCN.¹ We have therefore considered the sensitivity of computed cross-sections to reasonable variations in the potential, and this should provide some estimate of the reliability of the values presented here. Furthermore, it will allow for the reevaluation of these results as experimental data become available. Toward this latter end, we have also predicted pressure-broadening

¹ Data for a closely related rotational relaxation process have been obtained recently from microwave double resonance by Cohen and Wilson (1973). Their results are not directly comparable to our calculations since they worked at room temperature and examined vibrationally excited l -type doublets. Also, even with rather restrictive assumptions, e.g., $\Delta j \leq 3$, they were unable to uniquely invert the data to obtain rate constants. On the other hand, their results are consistent with ours; in particular, we both find a strong propensity for $\Delta j = 2$ transitions. Furthermore, they have measured pressure-broadening coefficients which, assuming that vibrational effects and changes with rotational level are small, are also in agreement with our computed values.

coefficients to compare with experiments currently under way in this laboratory; these are given in table 4.

The interaction potential was varied to examine (1) the region of the potential well and (2) the short-range anisotropies. The uniform electron gas model appears to predict a potential well which is somewhat deeper and at a separation somewhat smaller than the true minimum (Gordon and Kim 1972; Green 1974). Therefore, the ab initio potential was first modified by reducing the well depth by about 20 percent and moving it out about 0.3\AA ; the short-range and asymptotic long-range potentials were unchanged. Variations in the well are expected to affect cross-sections mostly in the low-energy (resonance) region. This was verified by scattering calculations (using a B6 basis) which showed virtually no changes in cross-sections above 60 cm^{-1} , but changes of 30-70 percent below 40 cm^{-1} . Pressure-broadening coefficients showed the same marked energy dependence, with changes of less than 5 percent above 40 cm^{-1} . To mimic uncertainties in the short-range potential, a seven-term Legendre fit was substituted for the 10-term fit. This increases the least-squares average deviation from 5 to 15 percent in the repulsive region but does not modify the well or the long-range potential. Scattering calculations were again repeated using a B6 basis, and cross-sections were found to change by typically 10-20 percent with no marked energy dependence between 15 and 140 cm^{-1} . Predicted pressure-broadening coefficients changed by less than 5 percent.

Based on the above calculations and on previous experience with similar calculations, the reliability of the rates in table 2 is conservatively estimated to be ± 50 percent for temperatures above 30°K and within a factor of 2 below 20°K . Pressure-broadening experiments should be a significant test at the higher temperatures since they provide a good measure of the short-range anisotropies. Unfortunately, such experiments cannot be performed for this system at temperatures low enough to significantly sample the potential well. The low-temperature results could be substantially improved by differential elastic-scattering measurements which would give information about the isotropic potential in the region of the well, and especially by spectroscopic data on the HCN-He van der Waals complex which could provide information about the anisotropic potential near the minimum.

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